BASICITY AND STRUCTURE OF α,β-UNSATURATED HETEROCYCLIC KETONES

V. Dibenzylidenecycloalkanones and Their Furan and Selenophene Analogs*

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The constants of the protolytic equilibrium and the displacement of the frequency of the stretching vibrations of the hydroxy group of phenol taking place under the influence of the formation of a hydrogen bond with the compounds studied have been measured for dibenzylideneacetone and dibenzylidenecycloalkanones (with five-, six-, and seven-membered rings) and their furan and selenophene analogs. It has been shown that the screening of the carbonyl group of the aliphatic ring creates considerable steric hindrance for the solvation of the carbenium ions formed in an acid medium, as the result of which the constants of the protolytic equilibrium fall on passing from compounds with an open chain to the cycloalkanone derivatives. The inclusion of a carbonyl group in a five-membered aliphatic ring creates more favorable conditions for conjugation than exist in analogous compounds with an open chain and in those with six- and seven-membered rings, in consequence of which the capacity for forming a hydrogen bond changes in the corresponding sequence.

In preceding communications [1-3] devoted to the study of the proton-accepting capacity of chalcone and its heterocyclic analogs and vinylogs, the hypothesis was put forward that in some cases of steric hindrance the solvation of the carbenium ions formed in an acid medium plays a fundamental role. In view of this, it appeared of interest to compare the acid-base properties of dibenzylideneacetone (I) and its heterocyclic
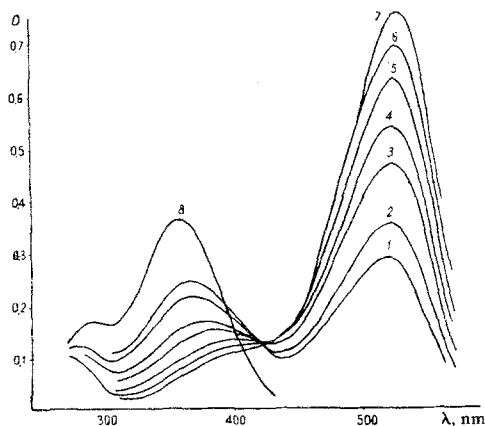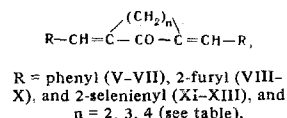

Fig. 1. Absorption curves of 2,7-diselenienylidenecylcopentanone in solutions of sulfuric acid in glacial acetic acid: 1) 5.89% H_2SO_4; 2) 7.18% H_2SO_4; 3) 10.38% H_2SO_4; 4) 13.25% H_2SO_4; 5) 17.75% H_2SO_4; 6) 22.88% H_2SO_4; 7) 32.31% H_2SO_4; 8) in glacial acetic acid.

analogs (II)-(IV) with the properties of those α,β-unsaturated ketones in which the carbonyl group is

screened by aliphatic rings of different sizes of the type:

$$R-CH=C \overset{\displaystyle (CH_2)_n}{\underset{\displaystyle}{-CO-C}}=CH-R,$$

R = phenyl (V-VII), 2-furyl (VIII-X), and 2-selenienyl (XI-XIII), and n = 2, 3, 4 (see table).

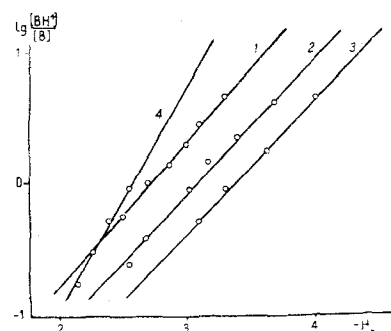Since the specific solvation of carbenium ions must take place mainly about a coordination-unsaturated

Fig. 2. Log ($[BH^+]/[B]$) as a function of $-H_0$ for: 1) dibenzylideneacetone (I); 2) 2,5-dibenzylidenecyclopentanone (VI); 3) 2,6-dibenzylidenecyclohexanone; 4) difurfurylideneacetone (II).

carbenium atom, the inclusion of the carbonyl group in an aliphatic ring, which screens the carbenium atom in the corresponding ions, must create serious steric hindrance to the solvation of the ionic form of the ketones. However, this change in the chemical structure of carbonyl compounds must necessarily affect not only the solvation energy of the ions but also the transfer of electronic effects in these molecules [4]. Thus, on passing from dibenzylideneacetone and its analogs to the corresponding cycloalkanone derivatives, two factors affecting the basicity of the ketones change: solvation and electronic effects, mainly the conjugation effect. In order to study the action of each of them individually, we have determined the basicity of the carbonyl compounds by two independent methods: a) spectrophotometrically in solutions of 100% sulfuric acid in glacial acetic acid; here the predominant role is played by the solvation energy of the molecules with ions; and b) by measuring the displacement of the characteristic frequency of the vibrations of the hydroxy group of phenol in the IR spectra ($\Delta\nu_{OH}$) [5-7] taking place under the influence of the perturbing action of a hydrogen bound formed with the carbonyl groups of the compounds investi-

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* For preceding communication, see [1].

Constants of the Protolytic Equilibrium K and Magnitudes of
$\Delta\nu_{OH}$ of the Compounds Studied

| Com-pound	Name	$(K \pm \Delta K) \cdot 10^5$	$\Delta\nu_{OH} \cdot cm^{-1}$
I	Dibenzylideneacetone	220 ± 10	252 ± 3
II	Difurfurylideneacetone	—	269 ± 3
III	Dithienylideneacetone	1010 ± 60	256 ± 3
IV	Diselenienylideneacetone	1300 ± 100	263 ± 3
V	2,5-Dibenzylidenecyclopentanone	85 ± 4	274 ± 4
VI	2,6-Dibenzylidenecyclohexanone	45 ± 1	218 ± 2
VII	2,7-Dibenzylidenecycloheptanone	7.6 ± 0.3	216 ± 2
VIII	2,5-Difurfurylidenecyclopentanone	—	272 ± 2
IX	2,6-Difurfurylidenecyclohexanone	—	234 ± 2
X	2 7-Difurfurylidenecycloheptanone	—	232 ± 2
XI	2,5-Diselenienylidenecyclopentanone*	780 ± 50	—
XII	2,6-Diselenienylidenecyclohexanone	330 ± 20	—
XIII	2,7-Diselenienylidenecycloheptanone	186 ± 5	—

*$\Delta\nu_{OH}$ for the diselenienylidenecycloalkanones could not be measured because of their low solubility in carbon tetrachloride.

gated. In the latter case, the influence of solvation factors on the basicity of the ketones is reduced to a minimum.

In measuring the constants of the protolytic equilibrium of the compounds under study, we encountered some complications. In spite of the fact that the ketones studied exist in the molecular form in glacial acetic acid (the spectra of the acetic acid solutions are practically identical with those of their solutions in ethanol), the absorption curves in acetic acid do not, as a rule, pass through the isobestic point (Fig. 1). An analogous phenomenon is observed at high concentrations of sulfuric acid ($\sim 30\%$ and above) where practically constant protonation ("saturation") is reached for the majority of the compounds studied. These facts can be explained by the change in the composition of the solvate cloud with a change in the solvent. In addition, the observed slight bathochromic shift of the absorption curves of the ketones when the concentration of sulfuric acid is increased may be connected with a marked change in the physical properties of the medium on passing from glacial acetic acid with a low dielectric constant ($\varepsilon = 6.19$) to its mixtures with sulfuric acid ($\varepsilon_{H_2SO_4} = 115$ [8]).

In spite of the above-mentioned complications, the process of protonation of the compounds studied is described satisfactorily over a certain range of concentrations by Hammett's acidity function $H_0 = pK - \log [BH^+]/[B]$. This follows from a consideration of the dependence of $\log [BH^+]/[B]$ on H_0, which is expressed for the various substances studied by parallel straight lines with slopes approximating to unity (Fig. 2), which shows that the protonation process is described by the simplified equation:

$$B + H^+ \rightleftarrows BH^+$$
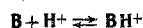
Exceptions are compounds containing a furan ring (for example, II and X) for which the corresponding slope considerably exceeds unity. It is possible that in these compounds partial protonation of the furan ring takes place.

A comparison of the constants of the protolytic equilibrium of dibenzylidene- and diselenienylideneacetones (I, IV) with the values of K for the corresponding derivatives of cyclopentanone VI and XI shows

that the inclusion of the carbonyl group in a five-membered aliphatic ring leads to a considerable decrease in basicity (on an average by a factor of 2, see table).

However, from the IR spectra for I and V and for II and VIII it can be seen that the inclusion of the carbonyl group in a five-membered aliphatic ring leads to an increase in $\Delta\nu_{OH}$ and, consequently, to an increase in the basicity of the ketones. This undoubtedly is the result of an increase in the electron density on the oxygen of the carbonyl group due to an increase in the degree of conjugation in the molecule, which is shown by the observed bathochromic shift in the electronic spectra of the corresponding ketones [4]. The apparent inconsistency in the results of the determination of the relative basicity of the compounds obtained by the two different methods must be ascribed to the fundamental influence of solvation effects on the position of the protolytic equilibrium.

It follows from a consideration of the conformations of the cycloalkanes [9] that both on the formation of a hydrogen bond and in the process of protonation of the carbonyl group the approach of the reagents to the oxygen atom should not encounter steric hindrance from the side of the ring atoms. However, so far as concerns the steric effects arising in the solvation process, for carbenium ions it must be considerably greater than for the corresponding molecules, since the carbenium carbon atom is screened by the aliphatic ring to a greater extent than the oxygen atom of the carbonyl group around which the solvation of the molecular form mainly takes place. On this basis it is possible to assume that in a number of the compounds studied the changes in the solvation energy of the molecules are considerably smaller than the changes in the solvation energies of the corresponding ions, and to a certain approximation it is possible to take into account only the steric hindrance of the solvation of the carbenium ions.

Thus, the fact that the constants of the protolytic equilibrium of the ketones containing a five-membered aliphatic ring are lower than those of the corresponding compound with an open chain, while the opposite situation is found for $\Delta\nu_{OH}$, confirms the existence of steric hindrance to the solvation of the carbenium ions from the side of the aliphatic ring and its great influence on the position of the protolytic equilibrium.

With an increase in the size of the aliphatic ring, i.e., on passing from compounds of the cyclopentanone series to cyclohexanone and cycloheptanone derivatives, a further decrease in the constants of protolytic equilibrium is observed (compare V, VI, and VII, and XI, XII, and XIII). A particularly sharp fall in the basicity is found when the carbonyl group is included in a seven-membered ring—ten- to thirtyfold as compared with the corresponding ketones not containing an aliphatic ring (compare I and VII, and IV and XIII). This, in our opinion, may be connected with the fact that, as has been shown [4], the conditions for conjugation in six-membered and, particularly, seven-membered cyclic systems sharply deteriorate, in view of which the electron density on the oxygen atom of the carbonyl group and the proton-accepting capacity of the ketones fall. Furthermore, the weakening of the conjugation in the molecules and the decrease in the delocalization of the positive charge connected with it must lead to a fall in the solvation energy of carbocations with six- and seven-membered rings as compared with the cations of the cyclopentanone derivatives. In the latter, the positive charge is largely delocalized over the carbon atoms of the aromatic and heterocyclic rings that are not screened by the aliphatic ring, which facilitates solvation. It is possible that the steric hindrance to the solvation of the carbenium ions of cyclohexanone and cycloheptanone derivatives also arises as a consequence of the existence of these rings in nonplanar conformations.

From the shift in the frequency of the stretching vibrations of the hydroxy group of phenol on the formation of a hydrogen bond with the ketones ($\Delta\nu_{OH}$), the cyclohexanone derivatives (VI and IX) and the cyclopentanone derivatives (VII and X) have a considerably lower basicity than dibenzylideneacetone and its analogs, which may be ascribed to the worsening of the conditions for the conjugation of the carbonyl group with the exocyclic double bonds. Moreover, the cyclohexanone and cyclopentanone derivatives scarcely differ from one another in their capacity for forming hydrogen bonds, i.e., in their basicity. It would appear that ketones with a seven-membered ring should, for the reason given above, have a considerably lower basicity than the cyclohexanone derivatives. There are apparently some additional factors favoring an increase in the basicity of the cyclopentanone derivatives as compared with the cyclohexanone series and leading to a leveling out of their basicities. These probably include, in the first place, a decrease in the Bayer strain, in consequence of which, as is well known, in the cycloalkanones (C_4–C_7) an increase in the dimensions of the rings leads to an increase in basicity, both according to the shift in the frequency of the vibrations of the O–D bond of deuteriomethanol when it forms a hydrogen bond with the ketones [10] and according to determinations of pK_a in concentrated sulfuric acid solutions [11]. It is interesting that the dipole moments of 2,6-dibenzylidenecylcohexanone and 2,7-dibenzylidenecycloheptanone that we found, the magnitudes of which are determined mainly by the moment of the carbonyl group, are practically the same

(3.09 D and 3.10 D, respectively), which shows the approximate equality of the polarities of the C=O bonds in these compounds. For the heterocyclic analogs of dibenzylideneacetone (I), II–IV, there is no steric hindrance to the protonation of the carbonyl group and the solvation of the carbenium ions nor to the formation of a hydrogen bond from the side of the neighboring heterocyclic rings, and the effect of the field and, to a considerable extent, the induction influence of the heteroatom are eliminated. A comparison of the constants of the protolytic equilibrium and the magnitude of $\Delta\nu_{OH}$ for compounds I–IV shows that the sequence of changes in the positive dynamic effect of the conjugation of five-membered heterocyclic radicals found previously (2-furyl > 2-selenienyl > 2-thienyl) [1, 6, 12] is also observed in the heterocyclic analogs of dibenzylideneacetone.

A comparison of the basicity constants and $\Delta\nu_{OH}$ for dibenzylideneacetone (I) and chalcone [1, 2, 6, 12] ($K = 6.2 \times 10^{-5}$, $\Delta\nu_{OH} = 206$ cm^{-1}), for difurfurylideneacetone (II) and 1,3-bis(2-furyl)propenone ($\Delta\nu_{OH} = 245$ cm^{-1}), for dithienylideneacetone (III) and 1,3-bis(2-thienyl)propenone ($K = 55 \times 10^{-5}$, $\Delta\nu_{OH} = 214$ cm^{-1}), and for diselenienylideneacetone (IV) and 1,3-bis(2-selenienyl)propenone ($K = 84 \times 10^{-5}$, $\Delta\nu_{OH} = 205$ cm^{-1}) shows that the introduction of a vinyl group into the molecule of chalcone and its analogs between the carbonyl group and the aromatic or heterocyclic nucleus leads to an increase in the basicity by an average factor of 20–30 and to an increase in $\Delta\nu_{OH}$ averaging 40–50 cm^{-1}. This observation confirms the conclusion that we drew previously [3] concerning the increase in basicity of α,β-unsaturated ketones with the introduction of a vinylene group.

EXPERIMENTAL

We prepared all the unsaturated ketones studied by methods described in the literature [4, 13–16] and carefully purified them by repeated crystallization.

The protolytic equilibrium constants were measured spectrophotometrically [2, 3] in solutions of sulfuric acid (100%) in glacial acetic acid at 23 ± 2° C in an SF-4 instrument. The method for preparing the solutions of the compounds studied for spectrophotometric investigation was modified somewhat. Weighted samples of the ketones (2–3 mg) were dissolved in 100 ml of glacial acetic acid and 2-ml portions of the solutions obtained were transferred by a pipette to 10-ml measuring flasks, after which solutions of sulfuric acid in glacial acetic acid (of definite concentration) were added up to the mark. The sulfuric acid contents of the solutions obtained were determined gravimetrically.

The values of $\Delta\nu_{OH}$ were measured in carbon tetrachloride solutions in an IKS-14 instrument, as described previously [6].

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